

## FLOATING GATE NITRIDATION

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## BACKGROUND OF THE INVENTION

The present invention relates to integrated circuits, and more particularly to  
10 nonvolatile integrated memories.

Fig. 1 shows a cross section of a stacked gate nonvolatile memory cell such as  
used in flash and non-flash electrically erasable programmable read only memories  
(EEPROM). Conductive floating gate 110, made of doped polysilicon, overlies  
monocrystalline silicon substrate 120. Silicon dioxide 130 insulates the floating gate  
15 from the substrate. N type source/drain regions 140 in substrate 120 are separated by P  
type channel region 150. Channel region 150 is directly below the floating gate.  
Dielectric 160 separates the floating gate from control gate 170 made of doped  
polysilicon.

The memory cell is read by applying a voltage between the regions 140, applying  
20 a voltage between one of the regions 140 and control gate 170, and detecting a current  
through the other one of the regions 140. The memory cell is written (programmed or  
erased) by modifying a charge on floating gate 110. Floating gate 110 is completely  
> insulated on all sides. ~~The~~<sup>To</sup> modify the charge on the floating gate, electrons are  
> transferred between the floating gate and ~~substrate~~<sup>the</sup> 150 through oxide 130. The electrons  
25 can be transferred by Fowler-Nordheim tunneling or hot electron injection. See  
"Nonvolatile Semiconductor Memory Technology" (1998) edited by W.D. Brown and  
J.E. Brewer, pages 10-25, incorporated herein by reference. The electron transfer  
requires a voltage to be established between the floating gate and a substrate region (the  
substrate region can be channel 150 or a source/drain region 140). This voltage is  
30 established by creating a voltage between the substrate region and the control gate. The  
control gate voltage is coupled to the floating gate. To reduce the voltage required to be  
created between the substrate region and the control gate, a high capacitive coupling is  
needed between the floating and control gates. A high specific capacitance (capacitance

per unit area) can be obtained between the floating and control gates by reducing the thickness of dielectric 160. However, dielectric 160 functions as a barrier to a charge leakage from the floating gate to the control gate. Therefore, dielectric 160 has to be a high quality, thin, uniform dielectric in order to provide good data retention (low leakage) and ensure a predictable high capacitive coupling between the floating and control gates.

Dielectric 160 can be silicon dioxide. Also, ONO (silicon dioxide, silicon nitride, silicon dioxide) has been used. See U.S. patent no. 4,613,956 issued September 23, 1986 to Peterson et al. Another option is a combination of silicon dioxide and oxynitride layers. Thus, according to U.S. patent no. 6,274,902, a silicon dioxide layer is thermally grown on floating gate polysilicon, and an oxynitride layer is deposited by LPCVD (low pressure chemical vapor deposition) on the silicon dioxide.

### SUMMARY

This section summarizes some features of the invention. The invention is defined by the appended claims that are incorporated into this section by reference.

In some embodiments of the present invention, before the dielectric 160 is formed, the top surface of floating gate 110 is nitrified to incorporate nitrogen atoms. The nitridation may involve ion implantation of pure nitrogen or nitrogen compounds into layer 110. Alternatively, the nitridation can be accomplished by exposing the surface of layer 110 to a nitrogen containing plasma. Other techniques, known or to be invented, are also possible.

After the nitridation process, silicon dioxide is thermally grown on the nitrified surface of layer 110. The nitrogen atoms in layer 110 slow down the oxidation process, so a more uniform silicon dioxide layer with fewer defects can be formed. Optionally, other dielectric layers (e.g. silicon nitride, silicon dioxide, oxynitride) are formed on the thermally grown silicon dioxide layer.

In some embodiments, dielectric 160 includes a top layer of silicon dioxide. The top silicon dioxide layer is nitrified to incorporate nitrogen atoms. The nitrogen atoms may be pure nitrogen or part of nitrogen compounds. The nitrogen atoms reduce the leakage current, thus improving the data retention. Some of the nitrogen may bind with silicon atoms of the silicon oxide layer to form silicon nitride. The silicon nitride has a higher dielectric constant than silicon dioxide, thus increasing the capacitive coupling between the floating and control gates.

Some embodiments combine the features described above, i.e. the nitridation of floating gate 110 and the nitridation of the top silicon dioxide surface of dielectric 160.

The invention is applicable to split gate memories and other flash and non-flash floating gate memories, known or to be invented. Other features of the invention are described below. The invention is defined by the appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a cross section of a prior art nonvolatile memory cell.

Figs. 2-7 show cross sections of nonvolatile memory cells in the process of fabrication according to some embodiments of the present invention.

## DESCRIPTION OF SOME EMBODIMENTS

Fig. 2 illustrates a cross section of a nonvolatile memory cell at an early stage of fabrication. Semiconductor substrate 120 (monocrystalline silicon or some other material) is processed to form a suitably doped channel region 150 (type P in Fig. 2, but an N type channel can also be used). Dielectric 130 is formed on substrate 120 over channel 150. Dielectric 130 may be thermally grown silicon dioxide or some other type of dielectric. Then polysilicon layer 110 is deposited and doped during or after deposition. See for example U.S. patent application 09/640,139 filed August 15, 2000 and incorporated herein by reference.

The top surface of polysilicon 110 is nitrided to incorporate nitrogen atoms. The nitrogen atoms may be pure nitrogen or part of nitrogen compounds. In one embodiment, nitrogen is implanted by ion implantation to a dose of  $10^{13}$  to  $10^{15}$  atoms/cm<sup>2</sup> at an energy 1-30 keV. Optionally, the structure is thermally annealed. In one embodiment, the anneal is performed at 850-1000°C for 10 to 60 seconds.

In another embodiment, nitridation is performed with plasma. For example, remote plasma nitridation (RPN) can be used. RPN involves exposing the layer 110 to high density nitrogen plasma generated outside of a chamber containing the wafer. See U.S. patent 6,268,296 and U.S. patent publication 20010021588, both incorporated herein by reference.

In one embodiment, RPN is performed in a system of type Centura® available from Applied Materials, Inc. of Santa Clara, California. Suitable process parameters are:

Wafer temperature	300-500°C
Pressure	1-100 torr
Nitrogen (N <sub>2</sub> )	0.5 slm (standard liters per minute) to 5 slm
Helium (He)	1-6 slm
Time	10-600 seconds

Other parameters can also be used.

Optionally, a thermal anneal is conducted. For example, the structure can be held at 900-1100°C at a pressure of 1 to 500 torr in the atmosphere of any of N<sub>2</sub>, He, NO, O<sub>2</sub>, N<sub>2</sub>O, or a combination of these gases. An exemplary anneal time is 10-150 seconds.

Another suitable plasma nitridation process is decoupled plasma nitridation (DPN) performed in a machine of type Gate Stack™ Centura® available from Applied Materials, Inc. of Santa Clara, California. A similar machine, a Decoupled Plasma Source of type Centura®, is described in U.S. patent no. 6,074,954 issued on June 13, 2000 to Lill et al. and incorporated herein by reference. Exemplary process parameters are:

Power on the coil outside the processing chamber	100-500 W
Pressure	10 mTorr to 10 Torr
N <sub>2</sub> flow	50 sccm to 2 slm
Time	10-100 seconds

Optionally, the structure is annealed. The anneal parameters described above for the RPN process are suitable.

After the nitridation step, the exemplary surface concentration of nitrogen atoms is 1-20 atomic percent in some embodiments. The exemplary thickness of the nitrated layer 110.1 at the top of layer 110 is below 3 nm. These parameters are not limiting.

As shown in Fig. 2, the nitridation can be performed before the layer 110 is patterned. Alternatively, the nitridation can be performed after this layer is patterned. The nitridation can be a blanket process, or a mask can be used to block nitrogen from

some wafer regions. In the floating gate regions, both silicon and nitrogen atoms are present at the top surface of layer 110.

Then silicon dioxide 310 (Fig. 3) is formed by thermal oxidation or chemical vapor deposition (CVD) on the nitrated surface of layer 110. Thermal oxidation can be performed at 800-1050°C in an oxygen or oxygen/hydrogen atmosphere. In some embodiments, the thermal oxide growth rate is up to 10 times less than for a non-nitrated silicon surface. An exemplary thickness of layer 310 is 3 to 8 nm. Other thicknesses, processes, and process parameters may also be used. Fig. 3 shows the layer 310 to be on top of nitrated layer 110.1. In fact, some or all of the silicon atoms in layer 110.1 can be consumed by the oxidation process. A layer of silicon dioxide with  $\text{Si}_x\text{N}_y$  molecules can form as a result.

sub A2 Known techniques can be used to complete the memory fabrication. In the example of Fig. 4, silicon nitride layer 410 is formed by low pressure CVD (LPCVD) on layer 310. Silicon dioxide 420 is deposited by CVD, or thermally grown, on layer 410. Layers 310, 410, 420 are referenced as 160. Doped polysilicon 170, or some other conductive material, is deposited to provide the control gates (possibly wordlines each of which provides the control gates for a row of memory cells). The layers 170, 420, 410, 310, 110, 130 are patterned as needed. Source/drain regions 140 are formed by doping. Additional layers (not shown) may be formed to provide select gates, erase gates, or other features. See the aforementioned U.S. patent application 09/640,139 for an exemplary memory fabrication process that can be modified to incorporate the floating gate nitridation described above.

In Fig. 5, the nitridation of floating gate polysilicon 110 is omitted. Silicon dioxide 310 is formed on polysilicon 110 using conventional techniques (e.g. thermal oxidation or CVD). Then silicon nitride 410 is deposited. Silicon dioxide 420 is deposited by CVD or grown thermally on nitride 410. An exemplary thickness of layer 420 is 3-8 nm. Layers 310, 410 can be omitted or replaced with other dielectric layers.

The top surface of oxide 420 is nitrated to improve the data retention. The capacitance is also increased as nitrogen binds with silicon to form silicon nitride. The nitridation can be performed, for example, by ion implantation, RPN or DPN, using the processes described above for nitridation of polysilicon 110. A thermal anneal can be performed at the end of the nitridation as described above for layer 110.



In some embodiments, the surface concentration of nitrogen atoms is 1-20 atomic percent, and the thickness of the nitrided layer 420.1 at the top of layer 420 is below 3 nm.

Conductive layer 170 (Fig. 6), for example, doped polysilicon, is formed on the nitrided surface of oxide 420 as described above in connection with Fig. 4. This layer will provide the control gate. The structure is patterned and the fabrication is completed as described above in connection with Fig. 5.

In Fig. 7, the techniques of Figs. 2-6 are combined. Floating gate polysilicon 110 is nitrided as described above in connection with Fig. 2. Then one or more dielectric layers are deposited (e.g. oxide 310, nitride 410, and oxide 420), with the top layer being silicon dioxide. The top silicon dioxide layer 420 is nitrided as described above in connection with Fig. 5. Then conductive layer 170 is formed and the fabrication is completed as described above.

Nitridation of floating gate polysilicon 110 and/or silicon dioxide 420 does not lead to a significant change in the total physical thickness of dielectric 160. However, the specific capacitance between the floating and control gates increases by 5 to 20% in some embodiments depending on the nitridation conditions. Other capacitance parameters can also be obtained.

The memory cells of Figs. 4, 6, 7 can be operated like the memory cell of Fig. 1. The memory can be programmed by Fowler-Nordheim tunneling of electrons from channel 150 or source/drain region 140 to floating gate 110. The memory can be erased by Fowler-Nordheim tunneling of electrons from the floating gate to channel 150 or a source/drain region 140. In other embodiments, the memory is programmed by hot electron injection, and erased by Fowler-Nordheim tunneling. In still other embodiments, the memory is erased by tunneling of electrons from the floating gate to a separate erase gate (not shown). Other memory structures, including split gate structures with select gates, and other programming and erase mechanisms, known or to be invented, can also be used.

The invention is not limited to the embodiments described above. The invention is not limited to the particular nitridation techniques or process parameters, layer thicknesses, or other details. The invention is not limited to the particular shape of the floating and control gates or their positioning relative to each other. The invention is not

limited to particular materials. For example, polysilicon 110 can be replaced with amorphous silicon, monocrystalline silicon, or their combinations. Silicon dioxide (SO<sub>2</sub>) can be replaced, or mixed with, silicon monoxide (we will use the term "silicon oxide" to refer both to silicon dioxide and silicon monoxide). Other embodiments and variations are within the scope of the invention, as defined by the appended claims.

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